

The Interaction of Organic Vapors With Coal. II. The
Irreversible Sorption of Amines

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The Interaction of Organic Vapors With Coal.
II. The Irreversible Sorption of Amines¹

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Summary

The sorption of different amines on coals of various ranks has been investigated. In all cases examined to date the sorption is isothermally irreversible. Different hypotheses for explanation of the irreversible sorption are discussed and it is concluded that the most probable explanation is the formation of solvates stabilized by mechanical trapping of amine molecules in the gel structure of the coal. Experimental evidence in support of a trapped molecule hypothesis is presented.

Introduction

Amines have been used frequently in extraction studies on coal. It has been found that it is difficult to remove the last traces of amines from both extract and residue, and this behavior might be considered evidence that the amines have reacted chemically with coal. It is the purpose of this investigation to study the sorption of gaseous amines on coal, to determine whether chemisorption has taken place, and if chemisorption is involved to find the nature of the functional groups in coal responsible for the chemisorption.

Experimental

Apparatus: Sorption measurements were made gravimetrically using McBain-Baker balances. The apparatus had six tubes connected in series so that six different samples of coal could be studied at the same time under the same experimental conditions. The springs were made from Ni-Span-C wire, 0.005 inches in diameter. The sensitivities of the springs ranged from 1.55 to 2.98 milligrams per millimeter extension. With a cathetometer reading to 0.1 mm. and a sample weight of 200 milligrams the precision of measurement was about 0.1%. The pumping system was composed of a two-stage mercury diffusion pump backed by a mechanical pump. The system included a storage chamber for storing the liquid whose sorption was to be measured and a mercury manometer for reading the pressure. Mercury sealed stopcocks were used for isolating the balance chambers and the storage chamber. The entire apparatus was mounted in an air thermostat. The temperature of the thermostat could be varied from 35°C. to 50°C. and held at a given temperature $\pm 0.10^\circ$ for a period of weeks.

Chemicals: The samples of coal used were obtained in part from the stock of the Coal Research Laboratory and were furnished in part by the Pittsburgh-Consolidation Coal Company. Samples in the form of coarsely-grained material were ground by passage through a hammer mill. The samples thus ground were used unsieved in order to avoid separation of the petrographic components of the coal. Samples of pale crepe natural rubber, GRS-1502 synthetic rubber, pulverized rubber peels (reclaimed rubber) and hard rubber dust were furnished by the General Tire and Rubber Company. Samples of natural and synthetic rubber in the form of gum (unvulcanized) stock were washed repeatedly with methanol. Cured (vulcanized) rubber samples were refluxed with a mixture of ether, toluene, and methanol. Anhydrous Drierite was used as a sample of calcium sulfate. The iron pyrites used was a mineralogical specimen consisting of small cubes of pyrites held in a stone matrix. Some of the cubes were freed from the matrix and ground to provide the sample.

Pyridine, Baker, C.P., was redistilled and stored over Drierite. Methylamine, Eastman, was obtained and used as a 25% solution in water. Ethanolamine, Eastman, and Ethylenediamine, Matheson, Coleman and Bell, were redistilled before use. 2-Methoxyethylamine, Eastman, was received as a 56-70% solution in water; potassium hydroxide was added and the mixture refluxed. 2-Methoxyethylamine was distilled from the mixture and then redistilled over sodium metal.

Procedure: The samples of coal were weighed out to 0.1 mg. and allowed to stand overnight in a desiccator. The samples, after being reweighed and placed in the apparatus, were allowed to stand for one hour, with an atmosphere of air present, to come to the thermostat temperature. A reading of the spring length was taken. It was assumed that the weight of the sample had not changed during the hour waiting period. The next step was to evacuate the apparatus and to follow the sample weight (spring length) until constant weight was attained. Coal samples were allowed to stand in the vacuum for a minimum of one day although the samples usually attained constant weight in shorter periods of time.

Following evacuation, the balance compartments were isolated from the vacuum line and the chosen vapor admitted to the system at a pressure equivalent to a relative pressure of about 0.5. The samples were kept under these conditions until a constant weight was reached. Usually periods of 3 to 5 days were needed to get complete adsorption although in some cases several weeks exposure was required. Plots of weight, W , vs. time, t , made for each experiment aided in the determination of the weight at equilibrium. After determination of the equilibrium weight, the system was evacuated until the sample came again to a constant weight. Figure 1: is a schematic drawing of a typical plot of W as a function of time. W_0 is the initial weight of the sample. After vapor has been admitted to the system the weight of sample increases to some constant value. The increase in weight is called W_e , the equilibrium sorption. When the system is evacuated the weight of the sample rapidly decreases at first and then gradually falls to a constant value. For all the work described here the final sample weight was always greater than the initial weight, W_0 . The increase in weight after a completed cycle of sorption and desorption is called W_p (permanent sorption).

Experimental Results

As previously mentioned, all coals investigated showed an irreversible adsorption of amines. The values of the permanent sorption, W_p , in moles per gram for the sorption of 2-methoxyethylamine are given in Table I.

Table I
Permanent Sorption of 2-Methoxyethylamine on Coals

Coal	35°C. 10^{-4} moles/gram	50°C. 10^{-4} moles/gram
Pocahontas	3.7	3.6
Pittsburgh (Edenborn)	5.9	7.1
Spitsbergen	5.9	9.2
Anthracite (Pa.)	7.2	6.6
Cannel	10.5	9.2
Clover Splint	15.7	14.4
Illinois No. 6	19.1	18.3
Wyoming	29.3	30.2
Lignite (Kincaid)	34.6	36.7
Brown (German)	41.7	36.0

In examining these results it will be noted that for the higher rank coals the values of W_p do not parallel the rank. However, for lower rank coals the values of W_p parallel the rank, increasing as the rank decreases. The high values of W_p for low-rank coals is noteworthy, being around 4×10^{-3} moles per gram of coal; this figure corresponds to a permanent sorption of 0.3 grams of 2-methoxyethylamine per gram of coal or about 30% of the original weight of the dry coal. It will also be noted that W_p does not change much as the temperature is changed, and that W_p does not increase or decrease uniformly with increase in temperature.

The tenacity with which amines are held by the coal even under prolonged evacuation suggests that the amine is chemically combined with the coal. To check this hypothesis, additional experiments were made to determine the nature of the functional groups responsible for the irreversible adsorption. The following possibilities were considered:

1. The formation of solvates with the inorganic constituents present in the coal.
2. The reaction of amines with acidic groups (COOH, OH) present in the coal.
3. The reaction of amines with elemental sulfur in the coal.
4. The reaction of amines with thioether or disulfide groups.
5. A reaction of amines with conjugated systems such as $C=C-C=O$.
6. The formation of solvates stabilized by trapping.

Each of these possibilities will be considered in turn.

Inorganic Constituents: All coals contain mineral matter and the compounds which comprise the bulk of this mineral matter are iron pyrites, silicates, and iron and calcium salts (1). Since calcium salts are known to form ammoniates there

1. C. B. Marson and J. W. Cobb, Gas J., 171, 39 (1925)

is a possibility that amines form similar complexes. Several sorption experiments were made using ferrous sulfide (synthetic), iron pyrites (mineralogical) and calcium sulfate. The results are tabulated in Table II. All measurements were made at 35°C.

Table II
Sorption of Amines on Selected Mineral Constituents

Amine	Mineral	W_e (moles/gram)	W_p (moles/gram)
Ethylenediamine	FeS	0.2×10^{-4}	0.09×10^{-4}
"	FeS ₂	0.13	0.13
2-Methoxyethylamine	FeS ₂	0	0
"	CaSO ₄	6.64×10^{-4}	0.63

Inspection of the results in Table II shows that W_p is essentially zero for all samples although W_e is large for CaSO₄.

Acidic Groups: The acidic groups in coal are probably COOH and OH. As the carbonyl frequency in the infrared spectra is very weak (2) it may be concluded that

2. R. A. Friedel and J. A. Queiser, Anal. Chem., 28, 22 (1956)

the concentration of COOH in coal is very low. The reaction with amines would be of the type,

$$RH(s) + BNH_2(g) \rightarrow RNH_3B(s)$$

The equilibrium constant for this reaction is the product of a number of equilibrium constants involving solution in water, neutralization, etc. and data are insufficient for its evaluation. However, it can be shown that the equilibrium constant for the reaction involves the basic dissociation constant of the amine in water. Amines with large dissociation constants would be expected to have a large K for the above reaction and a greater probability that the salt formed would not be pumped off under high vacuum. The above fact suggests the following procedure. If a given type of coal is picked then treatment of this coal with amines of different basicity should give values of W_p paralleling to some extent the dissociation constant.

Experiments were made with Pittsburgh Seam (Edenborn) coal at 35°C. using amines dissolved in water or containing water. Under these conditions the coal samples are simultaneously adsorbing water and amine. The results are shown in Table III.

Table III
Permanent Sorption (W_p) of Amines on Pittsburgh Seam Coal (35°C.)

Amine	pK (H ₂ O-25°C.)	W_p (moles/gram)
Methylamine - H ₂ O	3.4	4.3×10^{-4}
Ethanolamine - H ₂ O	4.3	3.9 "
2-Methoxyethylamine - H ₂ O	4.6	6.0 "
Pyridine - H ₂ O	8.6	7.0 "

These data show that W_p actually increases as the basic strength decreases or the result opposite to that expected. The oxygen content of the coal is about 4×10^{-3} moles of oxygen atoms per gram of coal. Consequently adequate oxygen is present and salt formation cannot be eliminated on the basis of insufficient oxygen in coal.

Reaction with Sulfur: Amines are known to react with elemental sulfur but data on the nature of the reactions are not available. Although the content of elemental sulfur in coal is supposed to be small, it seemed desirable to do a few experiments on the amine-sulfur reactions. Accordingly the sorption of various amines on rhombic sulfur were measured. Sorption does occur and the color of the sample changes from yellow to deep orange and then to black during the course of the sorption. The reaction product appears to form a very tight coating over the unreacted sulfur as, even after reaction periods of six to seven weeks, the yellow color of unreacted sulfur can be seen through the bottom of the glass bucket carrying the sample. None of our experiments have gone to completion. Most of the sorption, 75% or more, is irreversible and values ranging from 0.72 grams of amine to 0.016 grams of amine per gram of sulfur were obtained. Methylamine showed the lowest permanent sorption and ethylenediamine the highest permanent sorption. Sorption of ethylenediamine corresponds to 0.5 moles of amine per mole of sulfur. Unless the elemental sulfur content of the coal is high, it does not seem possible to explain the irreversible sorption of amines on coal in this manner.

Reaction with Sulfide or Disulfide Bonds: If thio-ether or disulfide bonds are present in coal, such bonds might react with amines. To check this possibility the sorption of 2-methoxyethylamine on a series of Pittsburgh Seam coals of known sulfur content was measured. The coal samples used were from the following mines: Hendrix, Edenborn, Montour, Waterman, Pursglove and Moundsville. The total sulfur content of these coals ranged from 0.90% to 4.25%. The permanent sorption for these samples ranged from 5.1×10^{-4} to 15.1×10^{-4} moles of amine per gram of coal. The experimental values of W_p showed no correlation with the total sulfur, pyritic sulfur, sulfate sulfur or organic sulfur contents of the coals.

To determine whether any reaction of this type did occur under the experimental conditions used, the sorption of 2-methoxyethylamine on samples of cured and uncured rubber stocks was measured. The data are tabulated in Table IV.

Table IV	
Sorption of 2-Methoxyethylamine on Rubber (35°C.)	
Rubber	W_p (moles/gram)
Pale crepe (vulcanized)	1.8×10^{-4}
" " (unvulcanized)	0.8×10^{-4}
GRS-1502 (vulcanized)	$0.5 \times "$
GRS-1502 (unvulcanized)	$0.4 \times "$
Rubber peels (reclaim)	$1.4 \times "$
Hard, rubber dust	$3.8 \times "$

The permanent sorption on all samples is low. As vulcanized samples contain more sulfur than unvulcanized samples and as in vulcanized samples some of the sulfur is present as thioether or disulfide bonds it can be concluded that the reaction between amines and sulfur links is very slow at 35°C.

Reactions with Conjugated Systems: The system of particular interest is the quinones. Many different reagents are known to react with quinones under rather mild conditions. If the reagent being added is designated as RH, the reaction can be written as,

$$C=C-C=O + RH \rightarrow RC-C=C-OH$$

Among the compounds which undergo this reaction are amines, alcohols, and bisulfites. The sorption of methanol on coals of various ranks has been under investigation in this laboratory for several years. Although in these experiments coal samples have been exposed for periods of time as much as several weeks and at temperatures ranging from 30° to 45°C., all methanol sorptions determined to date have been reversible to better than 1%. These data indicate that the experimental conditions are not correct for methanol addition to coal or that the concentration of conjugated systems of the quinone type in coal is very small. Additional experiments have been made where samples of coal were treated with liquid reagents under conditions which would be expected to lead to the addition of bisulfites or methanol to quinones. No evidence of appreciable reaction as measured by increase in weight of the coal sample has yet been obtained. In these experiments, reacting, say coal with liquid methanol, the system is two-phased and this fact might explain the slowness of the reaction. On the basis of the data at hand, it does appear that the concentration of quinones in coal is small.

Solvates Stabilized by Trapping: As mentioned before, most solvates would be unstable at the low pressures prevailing during the desorption process. However, such solvates might show sufficient stability if the molecules are trapped in the gel structure. On this hypothesis the permanent sorption of amines is analogous to clathrate formation found with crystalline compounds. The values of W_p hence are kinetic and not equilibrium values for amine sorption.

Two types of experimental evidence can be sought to support such a hypothesis. First, if it can be shown that an inert organic molecule of high volatility is irreversibly held by the coal, then the trapped molecule hypothesis appears probable. Second, other polymer systems with functional groups of known inertness to amines might be expected to show the same behavior.

For an experiment of the first type diethylether was selected as the molecule which could be considered inert. Accordingly, the sorption of diethyl ether on Wyoming coal was measured at 35°C. The value of W_p for ether was 10×10^{-4} moles for gram coal, and while this value is substantially less than W_p for 2-methoxyethylamine, nevertheless ether is held by this coal very tenaciously. For an experiment of the second type the sorption of 2-methoxyamine on two natural polymers was measured at 35°C. The results are tabulated in Table V.

Table V Sorption of 2-Methoxyethylamine on Polymeric Materials		
Polymer	W_e (moles/gram)	W_p (moles/gram)
Cotton linters	13.8×10^{-4}	5.1×10^{-4}
Raw silk	10.5 "	5.5 "

One other piece of evidence may be cited as supporting the trapped molecule hypothesis. For a series of coals, W_p was measured at 25°C. Keeping the samples under high vacuum, the thermostat temperature was changed successively to 40, 45 and 50°C. allowing the samples to remain at each new temperature for a minimum period of 24 hours. Under this procedure, W_p decreased slightly as the temperature increased. For a given coal, the values of $\log W_p$ when plotted against $1/T$ gave a straight line whose slope is related to the heat of reaction. Of the six coals on which this procedure was tried, anthracite gave the lowest heat of reaction, 1.3 kcal. per mole, and Clover Splint gave the highest heat of reaction, 3.3 kcal. per mole. These thermal values are much too low to be associated with anything but a very low order of bonding.

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